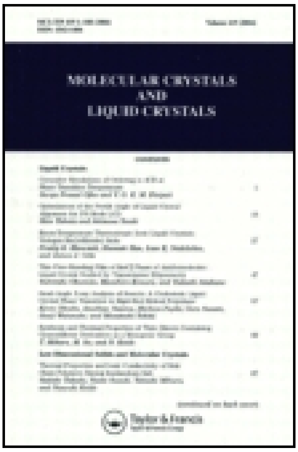

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

ESR Study and Deuteration Effect on the Magnetic Property of Hydrogen-Bonded Benzimidazole Nitronyl Nitroxide

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To cite this article: Hideaki Nagashima, Munetoshi Irisawa, Naoki Yoshioka & Hidenari Inoue (2002): ESR Study and Deuteration Effect on the Magnetic Property of Hydrogen-Bonded Benzimidazole Nitronyl Nitroxide, Molecular Crystals and Liquid Crystals, 376:1, 371-376

To link to this article: http://dx.doi.org/10.1080/10587250210789

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 371-376
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1058-725X/02 $12.00 + .00

ESR Study and Deuteration Effect on the Magnetic Property of Hydrogen-Bonded Benzimidazole Nitronyl Nitroxide

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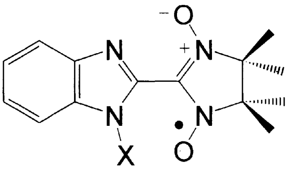
A solution ESR spectral investigation on 2-(benzimidazol-2-yl)-4,4,5,5-tetramethyl-1*H*-imidazoline-1-oxyl-3-oxide (= BIm-NN) and a magnetic susceptibility measurement of its –(N)H deuterated sample (BIm-NN-d_1) were carried out. A moderate amount of spin density was observed in benzimidazole ring bearing a hydrogen-bonding site. There was no appreciable difference in the temperature dependence of magnetic susceptibility between BIm-NN and BIm-NN-d_1.

Keywords: nitronyl nitroxide; hydrogen bond; benzimidazole; magneto-structural relationship

INTRODUCTION

The research activity of molecule-based magnetic material has been grown dramatically for the last ten years [1,2]. Since the discovery of the first organic ferromagnet (*p*-NPNN) [3], nitronyl nitroxide has attracted much interest as a suitable spin center for designing purely organic magnetic materials. Many groups have synthesized various NN derivatives and evaluated magnetic properties in connection with their molecular arrangements. Meanwhile, hydrogen bond has been used to control the spatial position of radical molecule in the crystal lattice [4-6] as well as to propagate magnetic interaction [7,8]. If the control of molecular arrangement suitable for parallel spin alignment between SOMOs is realized, a strong intermolecular magnetic interaction can be envisaged.

We have reported a NN derivative having benzimidazole ring at the 2-position of NN group [9,10]. BIm-NN formed a hydrogen-bonded chain structure and showed a strong ferromagnetic interaction with J = +13 cm^{-1} along the chain, which has not been observed in other NN derivatives. In this paper, we reported the solution ESR spectrum of BIm-NN and magnetic susceptibility of BIm-NN-d$_1$ to estimate the contribution of intermolecular hydrogen bond to magnetic interaction pathway.



BIm-NN (X=H)

BIm-NN-d$_1$ (X=D)

FIGURE 1 Chemical structure of the radicals.

RESULTS AND DISCUSSION

Solution ESR spectra

It is essential to know how the spin density of an unpaired electron distributes within the radical molecules because an intermolecular magnetic interaction is dominated by the polarized spin density. The ESR spectrum of 2×10^{-5} M solution of the radical in benzene at room temperature consists of five main lines corresponding to the coupling of an unpaired electron with two equivalent nitrogen nuclei. If only the coupling of the unpaired electron to hydrogen nuclei of the four equivalent methyl groups was observed, each of the five lines will consist of thirteen lines at most. The high-resolution spectrum appears that each line contains sixteen lines implying the coupling of the electron to not only the twelve hydrogen nuclei but also the hydrogen and / or nitrogen nuclei of benzimidazole ring. The hyperfine coupling constants obtained by the non-linear curve fitting of the spectrum is summarized in TABLE 1. Two nitrogen nuclei of benzimidazole ring

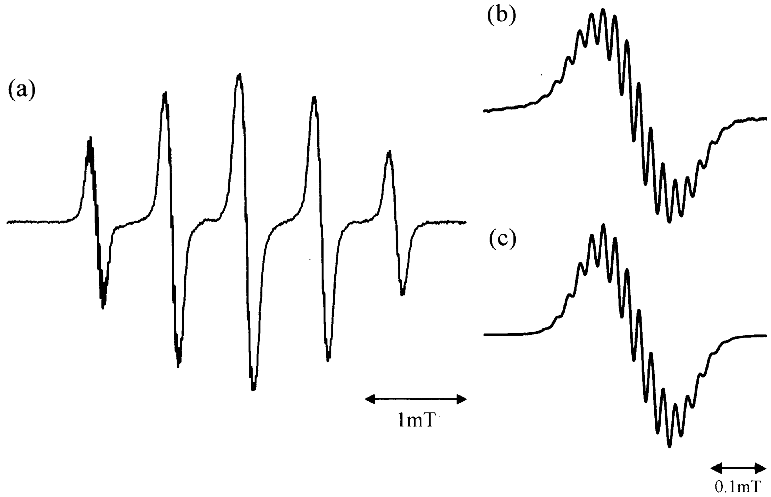


FIGURE 2 ESR spectra of BIm-NN in benzene (a); the line of the lowest field (b) and its simulation (c).

(=N– and –N(H)) were not equivalent as reported for benzimidazole-2-*tert*-butylnitroxide [11]. A moderate amount of spin density was observed on –N(H) nitrogen, which implied that a little spin was also polarized on –(N)H proton, though we cannot predict the sign of spin density. It also suggested the possibility of an intermolecular magnetic interaction through hydrogen-bonded pathway. Because of the restriction of isotopic rotation associated by an intermolecular hydrogen bond, the ratio of height and width of the spectrum was not as usual NNs' manner [12,13].

TABLE 1 Hyperfine coupling constant for BIm-NN in benzene at room temperature.

site	a / mT
nitroxide N	0.733
methyl H	0.021
benzimidazole =N–	0.043
benzimidazole –N(H)	0.012
benzimidazole 4, 5, 6, 7 C-H	0.017, 0.013, 0.005
or –(N)H	0.003, 0.002

Deuteration effect on magnetic property of BIm-NN

IR spectrum of BIm-NN showed a single strong band at 3160 cm^{-1}, assignable to a hydrogen-bonded N-H stretching vibration. BIm-NN-d$_1$, which was prepared by recrystallization from methanol-d$_1$ showed a hydrogen-bonded N-D stretching vibration at 2356 cm^{-1}, which shifted to about 75 % lower than that of BIm-NN as expected by the Hooke's law.

Compared with that of BIm-NN, temperature dependence of magnetic property of BIm-NN-d$_1$ was almost identical. The $(\chi_m T)_{max}$ value of BIm-NN was 1.68 emu K mol^{-1} at 3.2 K and BIm-NN-d$_1$ showed 1.72 emu K mol^{-1} at 2.7 K, suggesting that the effect of deuteration was revealed to be small (FIGURE 3).

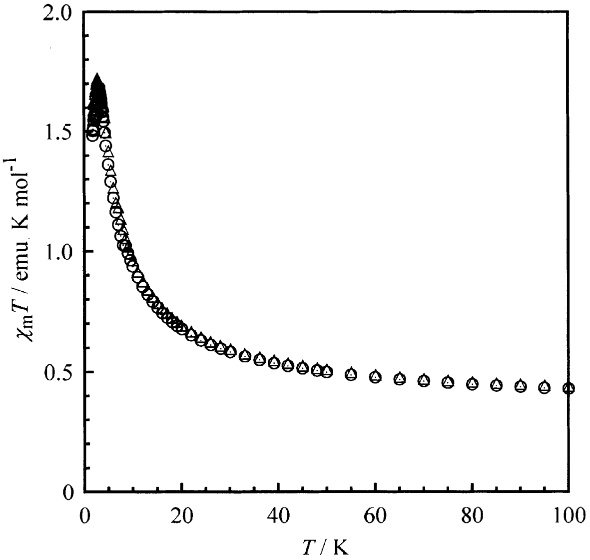


FIGURE 3 $\chi_m T - T$ plots for BIm-NN (○) and BIm-NN-d$_1$ (△) measured at 0.5 T.

In the previous paper [9,10], we proposed two plausible magnetic coupling mechanisms; (i) intermolecular coupling followed by the McConnell model (close contact between O and C of NN moiety), (ii) the spin polarization effect through hydrogen bond. When mechanism (ii) is predominant, it is expected to change magnetic interaction drastically by deuteration. These observations are in contrast to NNs with –OH hydrogen-bonding sites [4]. In BIm-NN, we considered that the mechanism (i) is effective on intermolecular interaction pathway because the deuteration effect for temperature dependence of $\chi_m T$ was small.

Acknowledgment

This work supported by Grant-in-aid for Scientific Research (No.3022392) from the Ministry of Education, Science, Sports and Culture of Japanese Government.

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